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Carbocatalysis by Graphene Oxide-based Nanomaterials in Organic Synthesis

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ABSTRACT

The emergence of graphene-based materials, such as graphene oxide (GO) and reduced graphene oxide (rGO), has revolutionized carbocatalysis in organic synthesis, offering a promising metal-free catalytic platform for diverse chemical transformations. This review critically examines the catalytic potential of GO and rGO in key organic reactions, including functional group modifications, coupling reactions, oxidations, reductions, and multicomponent processes. The inherent advantages of GO, such as high surface area, rich oxygen-functionalized basal plane, and superior dispersibility in polar solvents, are explored in the context of heterogeneous catalysis. Moreover, the review underscores the synthetic methodologies for graphene and its derivatives, analyzing their respective benefits and challenges while proposing strategies to overcome limitations in catalytic applications. The catalytic efficacy of GO and rGO nanosheets is further evaluated through comprehensive literature analysis, highlighting recent advances in the sustainable synthesis of pharmaceutically relevant scaffolds. The study concludes with prospective trends in graphene-based carbocatalysis, emphasizing its potential to foster environmentally benign, metal-free catalytic systems for targeted organic transformations.

Keywords: Carbocatalysis, Graphene oxide, Reduced graphene oxide, Nanocatalysis, Catalytic application, Organic synthesis, Metal-free catalysis.

INTRODUCTION

Historically, catalysis primarily focused on enhancing the activity and selectivity of catalysts, often overlooking recovery and reusability considerations. Conventional homogeneous organocatalysts, transition metal catalysts, and biocatalytic systems exhibit significant catalytic activity and selectivity, attributable to their molecular-level catalytic sites[1]. These single-site catalysts, being highly soluble in reaction media, offer exceptional reactivity and selectivity, even under mild conditions. However, their drawbacks include the use of expensive metal salts, costly ligands, labor-intensive purification processes, and challenges in catalyst recovery.

The discipline of organic synthesis, centered on the construction of complex organic molecules, has significantly evolved through strategic synthetic approaches. It underpins the development of pharmaceuticals, agrochemicals, and advanced materials, profoundly impacting various sectors, including medicine, agriculture, and industrial chemistry[2]. The evolution of organic synthesis is marked by a shift towards more sustainable, atom-economical, and environmentally benign methodologies, aiming to minimize waste and reduce the use of toxic reagents.

Despite substantial advancements in both homogeneous and heterogeneous catalysis, the quest for catalysts that deliver high activity, selectivity, and environmental compatibility persists. The development of single-step synthetic routes utilizing heterogeneous catalysts poses a considerable challenge, given the imperative to minimize energy consumption and processing time. This underscores the pressing need for catalysts that not only drive efficient chemical transformations but also facilitate straightforward separation and recovery of products.

Nanocatalysis

The synthesis of materials with high surface area remains a pivotal objective in heterogeneous catalysis, as surface-initiated pathways dominate these reactions. The nanoscale properties of materials, characterized by exceptionally high surface-to-volume ratios, have garnered considerable attention across diverse research domains, including biotransformation, fine chemicals, pharmaceuticals, and renewable energy[3]. Nanocatalysis research primarily aims to engineer catalysts with optimal selectivity, enhanced activity, minimal energy consumption, and prolonged stability. This necessitates precise control over the size, morphology, spatial distribution, surface composition, and electronic structure of nanocatalysts. To facilitate catalyst recovery and recycling, active nanomaterials are frequently anchored onto inert matrices, ensuring their separation from reactants post-reaction.

Beyond traditional metal catalysts, metal-free nanomaterials have emerged as promising candidates in heterogeneous catalysis. These include fullerene, graphite, graphene oxide (GO), carbon nanotubes (CNTs), and carbon nanodots (CNDs)[4]. Among these, GO exhibits significant catalytic potential due to its extensive surface area, rich oxygen-functionalized basal plane, and propensity for surface-mediated reactions[5]. The electronic interactions between GO and metal nanoparticles can activate dioxygen molecules, enhancing oxidation reactions. Consequently, selecting suitable supports for nanoparticle stabilization can be pivotal in optimizing reaction yields and product selectivity[6].

Carbocatalysis

Carbocatalysis, characterized by the utilization of carbon-based materials as catalysts, represents a paradigm shift toward metal-free catalysis[7]. Unlike conventional organocatalysts that consist of organic molecules, carbocatalysts are primarily composed of carbon, functioning as the active catalytic component. Historically, high-surface-area carbons, such as carbon black and activated carbon, have served as supports for metal catalysts, facilitating metal dispersion and adsorbing reactants near catalytic sites[8].

The advent of graphene (G) and graphene-based materials (G-mat) has further revolutionized carbocatalysis, establishing them as formidable metal-free catalysts. Graphene's 2D structure, coupled with its electronic conductivity and surface functionalization, renders it particularly suitable for catalyzing redox reactions, C–C bond formations, and multicomponent reactions[9]. While various carbon nanomaterials, including carbon nanotubes and diamond nanoparticles, exhibit catalytic potential, this review emphasizes the catalytic applications of graphene and graphene oxide as emerging carbocatalysts. For an in-depth exploration of CNTs and other carbon nanoforms in catalysis, readers are directed to comprehensive reviews on advanced carbon-based catalysts[10].

Synthesis of Graphene Oxide

Graphene oxide (GO) can be synthesized through various methods, each with distinct advantages and limitations[11,12]. The most widely employed methods for GO synthesis include the Hummers method, Staudenmaier method, and Tour method[13]. The initial investigation into the properties of graphite oxide was conducted by the British chemist B.C. Brodie in 1859[14]. Since then, the exceptional properties of graphite oxide have garnered considerable interest, leading to extensive research in the domain.

In Brodie's method, graphite was oxidized by reacting it with fuming nitric acid (HNO_3) and potassium chlorate ($KClO_3$) in a 1:3 ratio at 60°C for three to four days. Although effective, the method posed significant safety hazards due to the explosive nature of the KClO-HNO_3 mixture[14].

To mitigate these safety concerns, L. Staudenmaier modified Brodie's method in 1898 by partially replacing fuming nitric acid with sulfuric acid (H_2SO_4) and introducing incremental additions of $KClO_3$. Despite being less explosive, the process remained complex and hazardous[15]. Forty years later, Staudenmaier introduced a refined procedure, simplifying the oxidation steps without compromising the efficiency of GO synthesis.

In 1958, Hummers and Offeman presented a more practical and scalable method for GO synthesis, employing potassium permanganate ($KMnO_4$) as the primary oxidizing agent. The method involved mixing 300 g of $KMnO_4$, 2.3 liters of H_2SO_4, 50 g of sodium nitrate ($NaNO_3$), and 100 g of graphite powder[16]. The key innovation in Hummers' method was the replacement of $KClO_3$ with $KMnO_4$, reducing the risk of spontaneous explosions. Additionally, $NaNO_3$ was used to prevent fog acid formation. Despite its widespread adoption, the method generated toxic gases such as NO_2 and N_2O_4, necessitating further modifications.

Marcano *et al.,* advanced the conventional Hummers method by replacing $NaNO_3$ with a combination of H_2SO_3, H_3PO_4, and twice the amount of $KMnO_4$, significantly reducing the emission of hazardous gases[17]. This modified Hummers method not only improved safety but also produced GO with enhanced hydrophilicity, higher oxygen content, and comparable electrical conductivity.

Synthesis of Graphene Oxide Using the Modified Hummers Method

In the modified Hummers method, GO is synthesized from pure graphite powder through the following procedure:

1. **Preparation of Acid Mixture:**
   - A mixture of 27 mL of sulfuric acid (H_2SO_4) and 3 mL of phosphoric acid (H_3PO_4) (volume ratio 9:1) is prepared under constant stirring.
2. **Graphite Dispersion:**
   - 0.225 g of graphite powder is gradually added to the acid mixture under vigorous stirring.
3. **Oxidation Step:**
   - 1.32 g of $KMnO_3$ is slowly added to the graphite suspension while maintaining a controlled temperature to prevent excessive heat generation.
   - The mixture is stirred continuously for six hours, allowing the solution to turn dark green, indicating the formation of graphene oxide.
4. **Termination of the Reaction:**
   - To quench the reaction and eliminate excess $KMnO_4$, 0.675 mL of hydrogen peroxide (H_2O_2) is gradually added while stirring for ten minutes.
   - The exothermic reaction is allowed to cool to room temperature.
5. **Washing and Purification:**
   - 10 mL of hydrochloric acid (HCl) and 30 mL of deionized water (DIW) are added to the reaction mixture.
   - The mixture is then centrifuged at 5000 rpm for seven minutes using an Eppendorf Centrifuge 5430R.
   - The obtained residue is subjected to three additional wash cycles using HCl and DIW to ensure the removal of residual acid and impurities.
6. **Drying:**
   - The cleaned GO solution is transferred to a drying oven and maintained at 90°C for 24 h, yielding the final GO powder.

Catalytic Applications of Graphene Oxide (GO) and Reduced Graphene Oxide (rGO) in Organic Synthesis

Graphene oxide (GO) and reduced graphene oxide (rGO) nanosheets have garnered significant attention as carbocatalysts in organic synthesis due to their exceptional surface area, rich oxygen-functional groups, and unique electronic properties. This section reviews the catalytic applications of GO and rGO in various organic transformations, emphasizing group transfer processes, multi-component reactions, oxidations, reductions, and coupling reactions[18].

Before delving into specific catalytic applications, it is crucial to highlight the active sites on graphene-based materials, as these sites largely govern their catalytic activity.

Active Sites on Graphene-Based Materials

The catalytic activity of graphene-based materials is intrinsically linked to the presence of surface defects, oxygen-functionalized groups, and edge sites. These structural features not only influence the electronic properties of GO/rGO but also significantly impact their catalytic behavior in heterogeneous systems.

- **Basal Plane Functional Groups:** Epoxy, hydroxyl, and carboxyl groups on the basal plane serve as potential active sites for adsorption and catalytic activation of substrates.
- **Edge Defects:** Zigzag and armchair edge sites enhance catalytic performance by

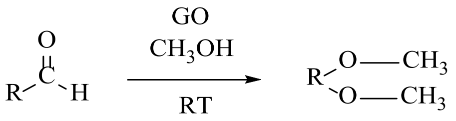
facilitating charge transfer and stabilizing reactive intermediates.

- π–π Interactions: Graphene's π-conjugated system enables π–π stacking with aromatic substrates, promoting interactions critical for specific catalytic transformations.

GO/rGO-Catalyzed Group Transformations

Acetylation of Aldehydes

Exfoliated graphene oxide has been reported to effectively catalyze the acetylation of aldehydes in methanol under ambient conditions. H. Garcia and colleagues demonstrated that GO, with its high surface area and accessible active sites, facilitates transition-metal-free acetylation, offering an environmentally benign catalytic system[19].

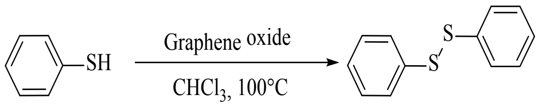


GO/rGO-Catalyzed Oxidation Reactions

GO, with its abundance of oxygen-containing functional groups, serves as a potent carbocatalyst for a variety of oxidation reactions. The oxygen functionalities provide multiple active sites for substrate activation and electron transfer, enabling selective oxidation processes.

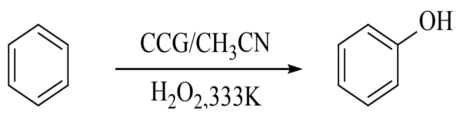
Oxidation of Thiols and Sulfides

Graphite oxide, an inexpensive and readily available heterogeneous catalyst, selectively oxidizes thiols to disulfides and sulfides to sulfoxides. This process avoids over-oxidation, maintaining high selectivity without the use of metal co-catalysts[20].



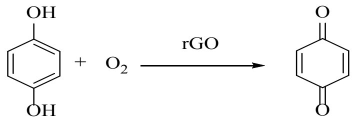
Oxidation of Benzene to Phenol

Ma *et al.,* reported that chemically converted graphene (CCG) acts as a highly effective and selective catalyst for the direct oxidation of benzene to phenol using hydrogen peroxide as the oxidant. The catalysts exhibited excellent stability, allowing for facile recovery and reuse without significant loss in activity[21].



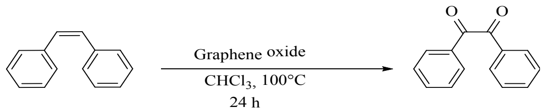
Transformation of Hydroquinone to Benzoquinone

In an aqueous system, Pei et al. investigated the oxidative conversion of 1,4-hydroquinone to 1,4-benzoquinone using reduced graphene oxide as a catalyst. The study highlighted that under neutral to acidic conditions, rGO effectively accelerates the oxidation rate, driven by electron transfer through its π-conjugated system[22].



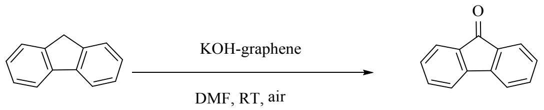
Oxidation of C–H Bonds

Bielawski and colleagues demonstrated the oxidation of olefins, diarylmethanes, and methylbenzenes using graphene oxide as a catalyst. The process was characterized by mild reaction conditions, absence of metal co-catalysts, and operational simplicity, underscoring the versatility of GO in oxidative transformations[23].



Oxidation of 9H-Fluorenes to 9-Fluorenones

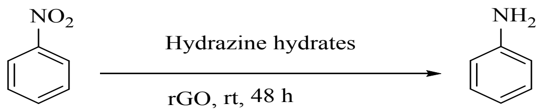
Graphene-supported KOH composites have been employed for the aerobic oxidation of 9H-fluorenes to 9-fluorenones in DMF at ambient temperature. Deng *et al.,* achieved high yields and high purity of the desired fluorenone products, demonstrating the catalytic potential of graphene nanocomposites in oxidative processes[24].



GO/rGO Catalysed Reduction Reactions

Hydrogenation of Nitrobenzene

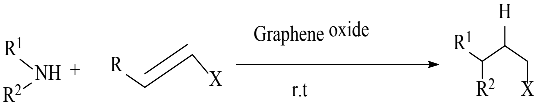
At room temperature, reduced graphene oxide was employed as a very effective and stable catalyst to reduce nitrobenzene. The zigzag edges of rGO may serve as catalytic active sites to aid in the activation of reactant molecules, according to Gao and his colleagues[25].



GO/rGO-Catalyzed Coupling Reactions

Aza-Michael Addition of Amines

GO has been successfully employed as a reusable organocatalyst for the Aza-Michael addition of amines to activated alkenes. Khatri *et al.,* developed a GO-catalyzed protocol for synthesizing amino-substituted compounds under mild conditions with reduced reaction times. This work represented the first documented coupling reaction utilizing GO as a carbocatalyst[26].

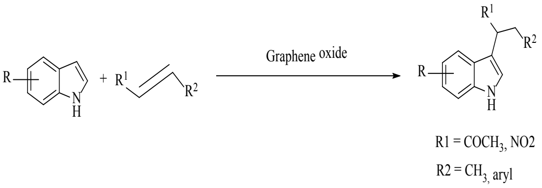


R = H, CH_3
R_1 = Et, n-Bu, n-Pr, Bz
R_2 = Et, n- Bu, n-Pr, Bz,
X = CN, $CONH_2$, $COOCH_3$

GO/rGO-Catalyzed Multicomponent Reactions

Friedel-Crafts Alkylation Reactions

Graphene oxide, with its oxygen-functionalized surface, acts as an acid catalyst in Friedel-Crafts alkylation. Szostak *et al.,* reported the first instance of GO catalyzing direct C–C bond formation via alkylation of arenes with styrenes and alcohols, producing diarylalkane derivatives under ambient conditions[27].



Knoevenagel Condensation

A covalently modified rGO catalyst, functionalized with an amino-terminated third-generation polyamidoamine (PAMAM) dendrimer, was utilized for the Knoevenagel condensation of benzaldehyde with dimethyl malonate. The rGO-PAMAM composite exhibited high catalytic activity and stability, enabling continuous dispersion in polar solvents and achieving high product yields[28,29].

CONCLUSION

In summary, this review underscores the catalytic versatility of graphene oxide (GO) and reduced graphene oxide (rGO) in advancing organic synthesis, positioning them as promising metal-free carbocatalysts for various functional group transformations. The structural features of GO and rGO, characterized by oxygen-rich functional groups, defect sites, and extended π-conjugated frameworks, provide a robust platform for catalytic applications, facilitating adsorption, electron transfer, and substrate activation.

The catalytic efficacy of GO/rGO spans a broad spectrum of organic reactions, encompassing oxidation, reduction, coupling, and multicomponent reactions. In oxidation processes, GO demonstrates exceptional catalytic performance, driven by its abundant oxygen functionalities that serve as active sites for selective transformations. The oxidation of thiols to disulfides and sulfides to sulfoxides exemplifies the efficacy of GO as a heterogeneous carbocatalyst, achieving high selectivity and yield under mild conditions. Similarly, the aerobic oxidation of benzene to phenol, mediated by chemically converted graphene (CCG), illustrates the strategic application of GO derivatives in oxidative transformations without the need for metal co-catalysts.

In reduction reactions, rGO emerges as a potent catalyst, leveraging its defect-rich surface and π-conjugated network to facilitate electron transfer. This is particularly evident in the hydrogenation of nitrobenzene to aniline, where the exposed zigzag edges and defect sites on rGO effectively activate the substrate molecules, enabling efficient reduction under ambient conditions. Furthermore, in coupling reactions, GO serves as a reusable organocatalyst in Aza-Michael additions and Friedel-Crafts alkylations, offering a sustainable, metal-free pathway for C–C bond formation.

The study also emphasizes the application of GO/rGO in multicomponent reactions, such as Knoevenagel condensation, wherein rGO-functionalized polyamidoamine (PAMAM) composites exhibit high catalytic stability and product selectivity. The integration of functionalized GO/rGO in such catalytic systems not only enhances dispersion and stability in polar solvents but also mitigates issues related to catalyst recovery and recyclability.

Despite the notable catalytic performance of GO and rGO, challenges remain concerning their scalability, control over oxidation levels, and stability under reaction conditions. Addressing these limitations requires further exploration into tailored functionalization strategies, optimization of synthetic protocols, and mechanistic studies to elucidate the precise role of active sites in catalytic processes.

Future research should focus on the rational design of GO/rGO-based catalysts, exploring synergistic interactions with other catalytic systems, and advancing green synthesis methodologies to minimize environmental impact.

Additionally, the development of cost-effective, scalable production routes for GO/rGO with controlled surface functionalities will be pivotal in expanding their industrial applicability, particularly in pharmaceutically relevant transformations and biomass valorization.

By consolidating the advancements in GO/rGO catalysis and identifying strategic directions for further investigation, this review underscores the transformative potential of graphene-based carbocatalysts in organic synthesis, aligning with the overarching goals of sustainable and environmentally benign chemical processes.

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Conflict of interest

The author declare that we have no conflict of interest.

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